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Use of Potassium Ferrate in Oxygen Demand Measurement

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USE OF POTASSIUM FERRATE IN OXYGEN DEMAND MEASUREMENT

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water. Conduct studies to determine the responses of aquatic organisms to water quality.
- Conduct an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

Many methods of measuring the oxygen demand of natural waters have been proposed. Each of these methods has manifested shortcomings of expense, accuracy, speed or reproducibility. The work described in this report was undertaken in an effort to devise a superior chemical method for total oxygen demand measurement.

Dwight G. Ballinger
Director
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ABSTRACT

This research project was initiated with the primary objective of improving the commonly used COD test by the use of ferrate(VI) ion as an alternate or preliminary oxidant. The oxidation of NH_3 and more general oxidation of organic compounds was desired. A secondary objective was the improved understanding of the mechanism of ferrate oxidations in dilute aqueous solutions.

The oxidation kinetics of water (phosphate-borate buffer) by ferrate ion were studied spectrophotometrically and by oxygen evolution measurements. It was found that the rate of water oxidation is expressed as follows:

$$\text{rate} = k_1[FeO_4^{=}] + k_2[FeO_4^{=}]^2$$

where both k_1 and k_2 are conditional rate constants and are dependent on hydrogen ion concentration.

The addition of solutes to the water before addition of ferrate ion speeds the disappearance of ferrate ion (spectrophotometrically) through the addition of a third term (k_3[solute]) to the rate law. In the case of most solutes, the values of k_1 and k_2 are not effected by the presence of the oxidizable solute. Ammonia, however, is an exception to this statement; acting to catalyze the oxidation of water. The actual oxidation of ammonia is a minor pathway.

The kinetics of ferrate oxidation of methanol, formic acid, ethanol, acetaldehyde, acetic acid, NTA, IDA, glycine, glyoxalic acid, oxalic acid,

triethylamine, diethylamine and piperidine were examined and are described herein.

The dichromate COD analysis was carried out on several samples, including phenol, lactic acid and sewage from the Lincoln, Nebraska sewage treatment facility. COD analysis was also carried out on sewage samples after prior treatment with potassium ferrate at pH 9. There was evidence that the ferrate ion actually stabilized organic materials originally refractory to the dichromate COD method but the oxidation of water (possibly catalyzed by sewage components) is too rapid to insure that the ferrate reacts quantitatively with the solute molecules. It is concluded, therefore, that the COD test can not be improved significantly by the incorporation of ferrate (VI) ion as an oxident.

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LIST OF TABLES

Number	Title	Page
1	Experimental First- and Second-Order Rate Constants for the Potassium Ferrate Oxidation of Water	19
2	Rate Constants for Ferrate Oxidation of Methyl Alcohol	20
3	Rate Constants for Formate Ion Oxidation by Ferrate Ion	21
4	Rate Constants for the Ferrate Oxidation of Nitrilotriacetic Acid	23
5	Rate Constants for Ferrate Oxidation of Iminodiacetic Acid	24
6	Rate Constants for Ferrate Oxidation of Glycine	25
7	Observed Rate Constants for Ferrate Oxidation of Glyoxylic Acid	26
8	Rate Constants for Ferrate Oxidation of Oxalate	27
9	Substrate Concentrations Needed for Rate of Oxidation to Equal Water Oxidation Rate	28
10	Resolved Rate Constants for Protonated Forms of Some Substrates	29
11	Rate Constants for Ammonia Oxidation by Ferrate Ion	30
12	Reaction Conditions and Values of k_{obs}, k_1^{PR} and k_2^{PR} for Reactions Between Potassium Ferrate and Various Amines	31
13	Rate Constants for Ethyl Alcohol Oxidation by Ferrate Ion	33
14	Rate Constants for Oxidation of Acetaldehyde by Ferrate Ion	34
15	COD Values for all Wastewater and Lake Water Samples	36

SECTION 1

INTRODUCTION

The Chemical Oxygen Demand (COD) of a water sample is a measure of the amount of molecular oxygen necessary to totally oxidize (forming CO_2) all of the organic compounds dissolved in the water. The COD value is actually measured by refluxing the sample with standard dichromate in sulfuric acid for two hours and then titrating the excess dichromate with a standard ferrous solution. The oxidation of many substrates by acidic dichromate is known to be less than quantitative even when appropriate catalysts are added.

Potassium ferrate(VI), K_2FeO_4, is an oxidizing agent that can be made inexpensively and which can oxidize many organic compounds, sometimes forming carbon dioxide, even when they are dilute solutes in water. In addition, water is also slowly oxidized to molecular oxygen, and ammonia is reportedly oxidized to molecular nitrogen by ferrate ion. The effective rate constants of each of these oxidations depends strongly on solution conditions, the most important variable being pH. For ferrate ion to be a useful adjunct to the COD determination, the rate of substrate oxidation must be much greater than the rate of water oxidation under the conditions of the oxidation. Whether this criterion is valid can be determined by a) measuring the rate of ferrate disappearance as a function of substrate concentration or b) measuring the rate of appearance of products specific to oxidation of solute or solvent. Both methods were utilized in this study.

SECTION 8

CONCLUSIONS AND RECOMMENDATIONS

Results of kinetic experiments and product analysis experiments indicated that ferrate ion is a useful reagent for the destructive oxidation of organic compounds dissolved in water. Its use as an auxiliary oxidant in the dichromate COD determination, however, is not recommended because there is no assurance that only the substrate molecules will be oxidized. To the contrary, the oxidation of water will always occur simultaneously and result in apparently high results. It is interesting that ferrate ion can partially oxidize some materials refractory to the dichromate COD analysis and render them as susceptible to dichromate oxidation.

Ferrate ion appears to have potential use in waste-water decontamination where the requirement for 100% oxidative efficiency is much less rigid. This use of ferrate ion should continue to be explored.

SECTION 3

EXPERIMENTAL PROCEDURES

PREPARATION OF REAGENTS

Potassium ferrate (K_2FeO_4) was prepared by the method of Thomson et. al. (1). The reprecipitated K_2FeO_4 was washed with isopropyl alcohol rather than ethyl alcohol as originally described. It was felt that this would be less susceptible to oxidation and thereby improve the purity of the recovered material. The purity of the product was assayed by the chromite method of Schreyer et. al. (2).

All water used in these studies was deionized water that had been distilled from glass. Water used in the COD measurements and the ammonia oxidation studies also was redistilled from alkaline permanganate prior to use.

The phosphate-borate buffer used was prepared by mixing two volumes of phosphate solution (0.271 F) with one volume of borate solution (0.166 F; 19.05 g $Na_2B_4O_7 \cdot 10H_2O$, 3.06 g H_3BO_3 in 600 ml). The final stock buffer solution was 0.181 F in phosphate and 0.0552 F in borate and the desired pH could be obtained by addition of NaOH or HNO_3. This mixture served as pH control and to prevent the precipitation of Fe(III) product as $Fe_2O_3 \cdot xH_2O$.

All reagents for COD assay were prepared as is common in such measurements (3). All other reagents used were reagent grade and were used as received.

METHODS OF MONITORING FERRATE OXIDATION REACTIONS

The rate of disappearence of ferrate ion can easily be monitored spectrophotometrically at 505 nm (ϵ = 1030 M^{-1} cm^{-1}). None of the oxidizable substrates studied absorb at this wavelength and the Fe(III) containing product has a very small molar absorptivity at this wavelength (ϵ = 20 M^{-1} cm^{-1}). The rate at which absorbance decreases, $-dA/dt$, is therefore proportional to the rate of disappearance of ferrate ion, $-d[FeO_4^{=}]/dt$. Those measurements were made at both conventional speeds (Cary 14 or B&L 600) and stopped-flow speeds (Durrum Gibson).

The final product of water oxidation is molecular oxygen. A Clark's type polarographic electrode and Yellow Springs Model 54 ARC oxygen meter was used to measure the rate of oxygen evolution ($d[O_2]/dt$) and the equilibrium oxygen concentration. These measurements were made in a cell of our design which was totally filled with deaerated sample into which could be injected a solution of K_2FeO_4. Presumably, the only source of O_2 is oxidation of water so these measurements are independent of the parallel oxidation of other solutes.

Gaseous reaction products (O_2, N_2, CO_2, N_2O, etc.) are readily detected and relative equilibrium concentrations determined by mass spectrometry. Reaction kinetics, however, can not be monitored by this method.

RATE OF OXIDATION OF WATER BY FERRATE ION

Murmann has reported (4) that the oxidation of water by ferrate ion proceeds via a complex path but he was not able to distinguish between a reaction three-halves order in ferrate and parallel first- and second-order reactions. By studying the reaction with a wide variety of ferrate concentrations and over a pH range of 7-10 it was clear that two parallel reactions

were responsible for the water oxidation. The rate law then is shown in eq. 1 where k_1 and k_2 are conditional rate constants dependent upon hydrogen ion concentration. Detailed evaluation of

$$\text{rate} = k_1[FeO_4^{=}] + k_2[FeO_4^{=}]^2 \quad (1)$$

$$\text{rate} = k_1'[FeO_4^{=}][H^+] + k_2'[FeO_4^{=}]^2[H^+]^{1.5} \quad (2)$$

the pH dependence allows equation 2 to be written where k_1' and k_2' are absolute rate constants at 25° and the ionic environment (phosphate-borate buffer) of the studies.

Numerical values of k_1 and k_2 are obtained from absorbance versus time data by measuring the actual rate of the reaction ($-d[FeO_4^{=}]/dt = (-dA/dt/\Delta\varepsilon b)$ at several points of known absorbance during the reaction. Solving eq. 3 simultaneously for two distinctly different times in the reaction gives values of k_1 and k_2.

$$\text{rate} \times \Delta\varepsilon b = \frac{dA}{dt} = k_1 A + \frac{k_2 A^2}{\Delta\varepsilon b} \quad (3)$$

In all cases, equation 3 is solved for at least two different pairs of rate-absorbance information from each reaction to check for internal consistancy.

Table I and Figures 1 and 2 include experimental values of k_1 and k_2. The hydrogen ion dependence of these values is analyzed and it is found that k_1 is first-order in hydrogen ion and that the k_1' has a numerical value of $1.9 \times 10^5\ M^{-1}\ sec^{-1}$ and that k_2 is approximately 1.5-1.7 order in hydrogen ion and has a numerical value of $(5.6 \pm 0.5) \times 10^{13}\ M^{-2.6}\ sec^{-1}$.

That equation 1 does indeed describe the rate law rather than the alternative proposed by Hurmann (eq. 4), initial reaction rates at constant pH

$$\text{rate} = k_{3/2}[FeO_4^{=}]^{3/3} \quad (4)$$

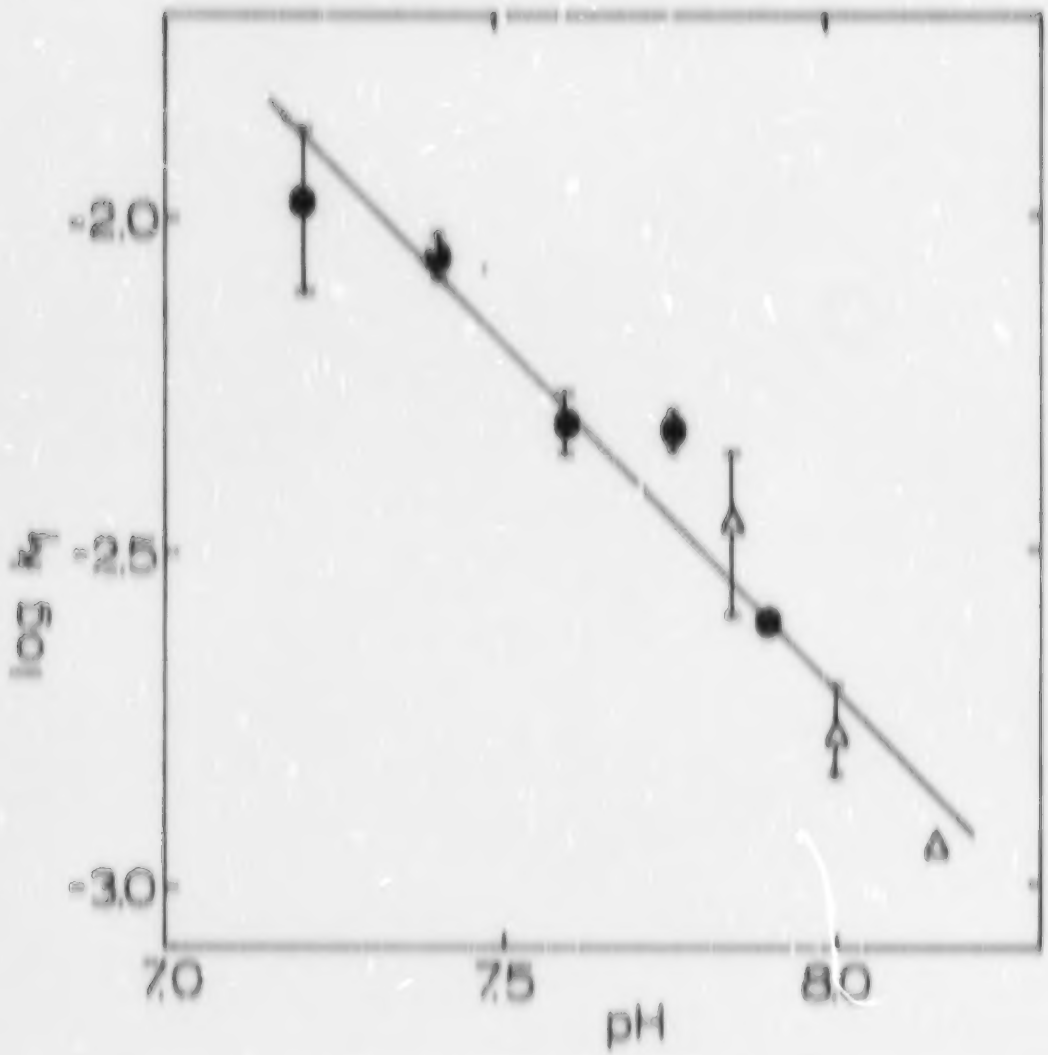

Figure 1. Potassium Ferrate Oxidation of Water.

Temperature = 25°C

● Goff and Murmann (4)

△ This study; Slope of all data = -1.04

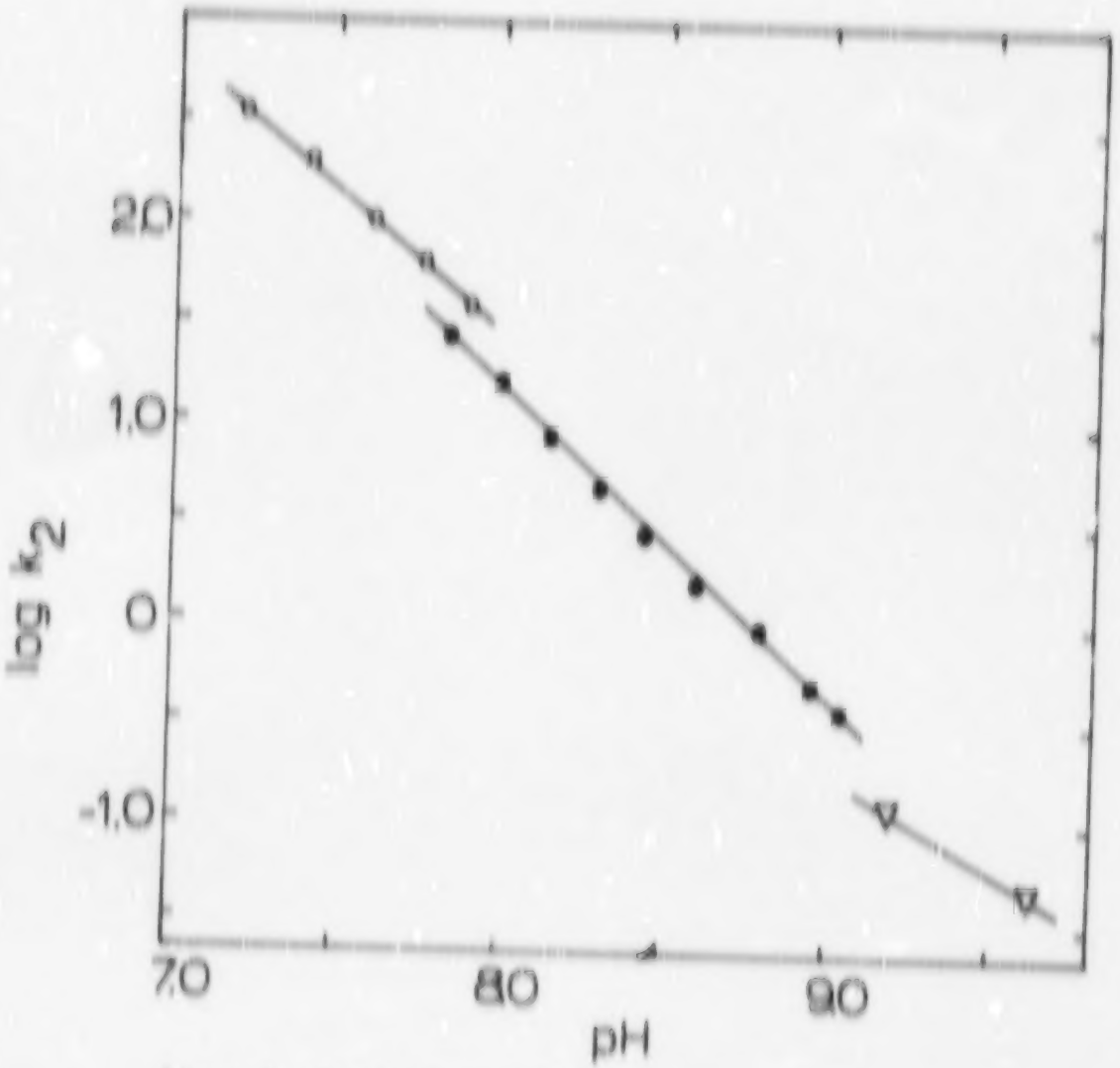

Figure 2. Potassium Ferrate Oxidation of Water.

- ⊖ Goff and Hurmann (4) Temp = 25°C; Slope = -1.39
- ● This study; Temp = 25°C; Slope = -1.57
- ▽ Magee (8) Temp = 25.32°C; Slope = -0.98 ± 0.2

were plotted versus $[FeO_4^{=}]^{3/2}$ (Fig. 3) and rate/$[FeO_4^{=}]$ was plotted vs. $[FeO_4^{=}]$ (Fig. 4). If eq. 4 describes the rate law, Fig. 3 should be a straight line with a zero intercept and Fig. 4 should show curvature. If, on the other hand, eq. 1 describes the rate law, Fig. 4 should be a straight line and Fig. 3 should be curved, possibly with a finite, positive intercept. That the latter case is shown to hold is evidence for equation 1 describing the rate law. In addition, when the water oxidation is studied at pH 8.95, a good second-order plot is obtained (Fig. 5). At this pH, the first-order term has become insignificant and virtually all of the ferrate ion disappears via the second-order term of eq. 1. Such behavior would be impossible if eq. 4 describes the rate law.

Limited studies were also made at 20°C (Table I) and, these values combined with the 25°C data lead to estimates of activation parameters as follows: for k_2; E_a = 14 Kcal/mole and log A = 11.

RATE OF OXIDATION OF SOLUTES BY FERRATE ION

General Strategy

The four sets of compounds studied are:

1. Compounds containing one carbon atom of increasing oxidation number (methanol, formaldehyde, formate ion)
2. Nitrilotriacetic acid (NTA) and its possible oxidation products (iminodiacetic acid (IDA), glycine, glyoxylic and oxalic acid, and ammonia)
3. Organic amines (triethylamine, diethylamine, pyridine, piperidine)
4. Compounds containing two carbon atoms, one of which shows increasing oxidation number (ethanol, acetaldehyde, acetate ion)

These four sets of compounds will be discussed sequentially.

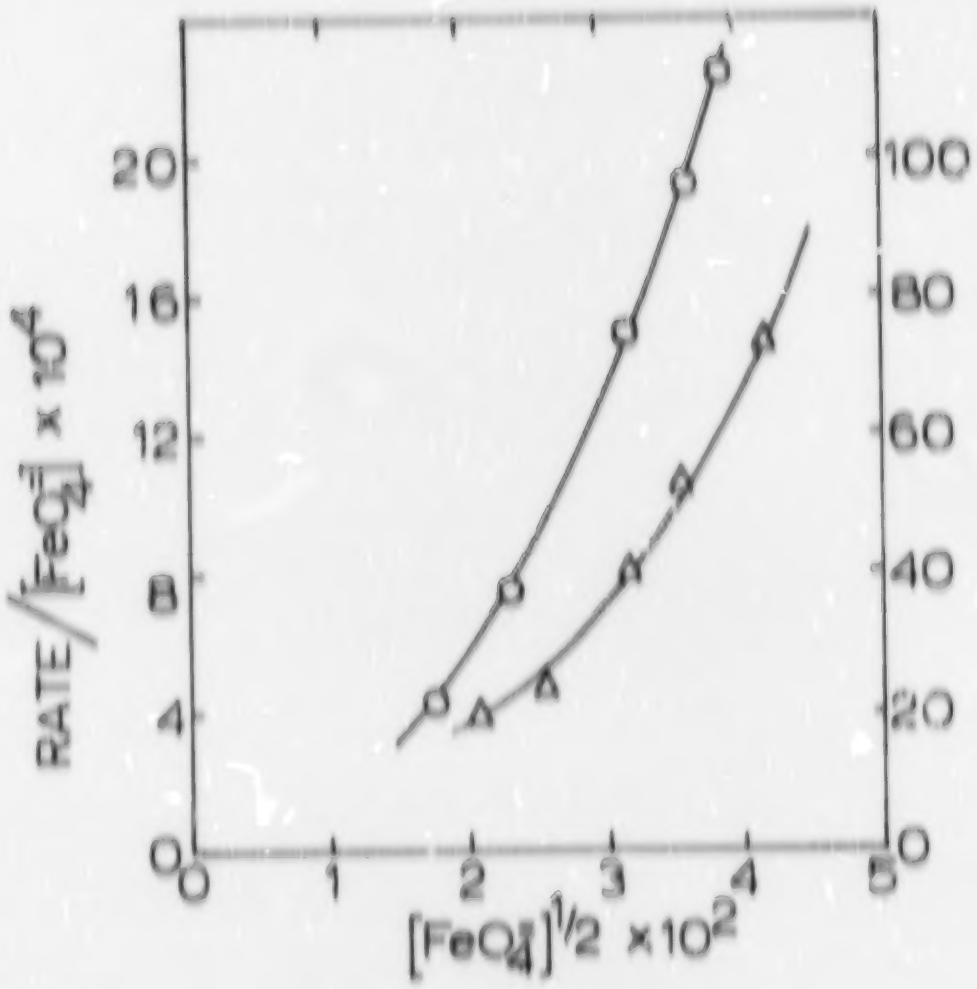

Figure 1. Initial rate data for potassium ferrate oxidation of water.

Temperature = 20°C

○ pH 8.45 (left axis)

△ pH 8.15 (right axis)

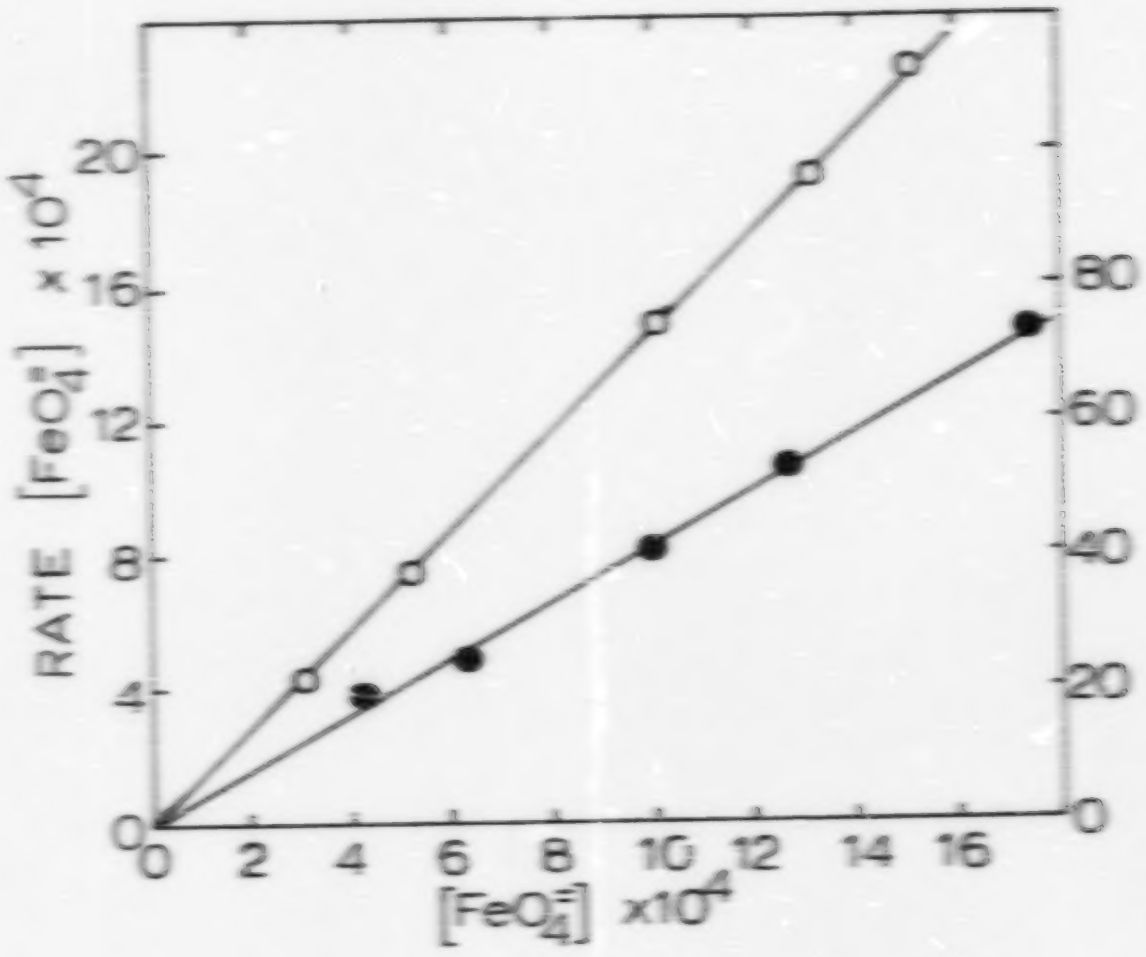

Figure 4. Initial rate data for potassium ferrate oxidation of water.

Temperature = 25°C

○ pH 11.45 (left axis) ● pH 11.15 (right axis)

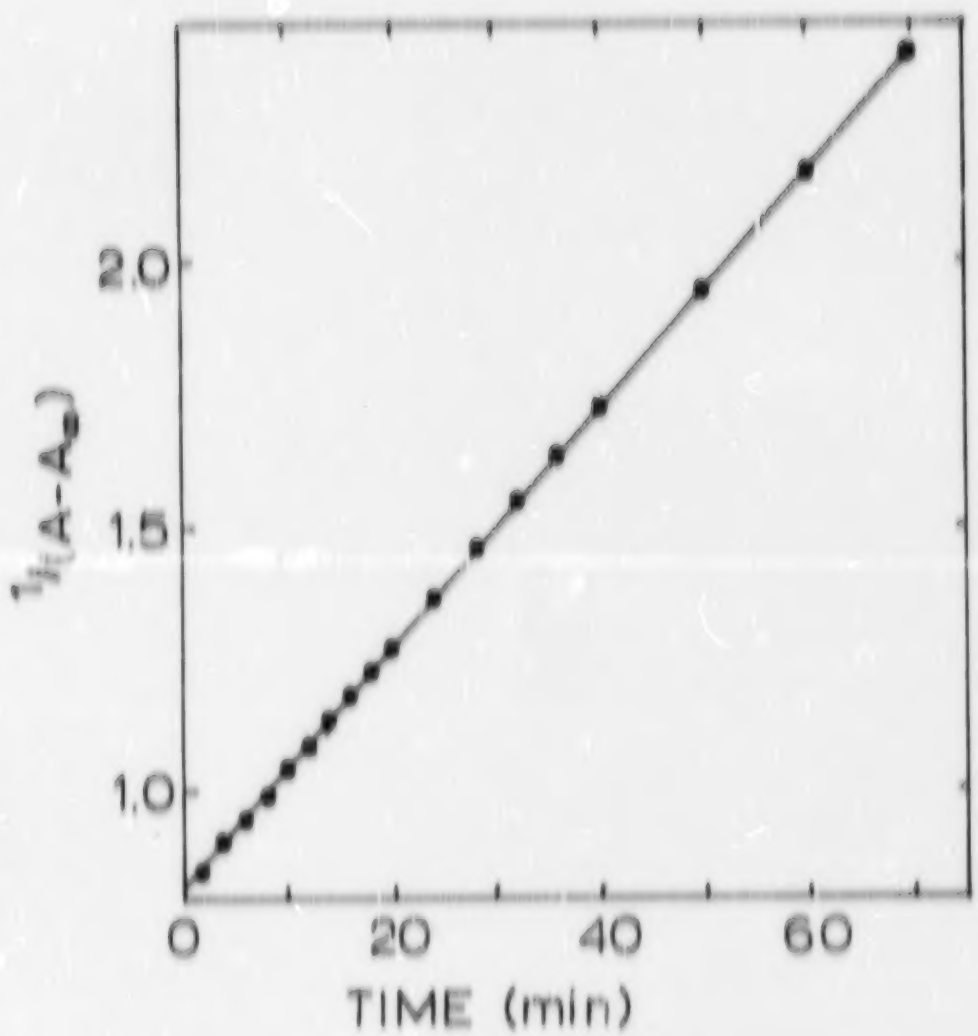

Figure 5. Second-order plot of potassium ferrate oxidation of water at pH = 8.95.

Run #96: $[FeO_4^{=}]_0 = 1.22 \times 10^{-3}$ F. Temp. = 25°C

One-Carbon Compounds

The oxidations of methanol and formate ion were examined closely and a few runs were made on formaldehyde. Both methanol and formate ion are oxidized in reactions which are first-rate in both ferrate ion and in substrate and which show important pH dependence. Neither compound seems to influence the rate of water oxidation which is occurring in parallel. Tables 2 and 3 include the conditional rate constants for these oxidations. The rate law then has the form of eq. 5 where "S" signifies the substrate or solute in question.

$$\text{rate} = k_1[FeO_4^{=}] + k_2[FeO_4^{=}]^2 + k_s[S][FeO_4^{=}] \quad (5)$$

$$= k_1'[FeO_4^{=}] + k_2[FeO_4^{=}]^2 \quad (5a)$$

$$k_1' = k_1 + k_s[S] \quad (5b)$$

The oxidation of formaldehyde must be measured by the stopped-flow method, and is much faster than either methanol or formate ion. The formaldehyde reactions at pH 8.6-9.6 appears to be first-order in ferrate but second-order in formaldehyde. The known aqueous chemistry of formaldehyde is quite complicated, involving hydration and polymerization (5). The details of the formaldehyde were not examined further.

When methanol is present in excess over ferrate ion, formate ion is the major product of the methanol oxidation. The amount of carbon dioxide (bicarbonate) formed is very minor in these cases as measured by a CO_2 electrode. However, when ferrate is added in excess, near-quantitative formation of CO_2 occurs.

NTA and its Oxidation Products

Various other studies have indicated that when NTA (nitrilotriacetic acid) or related compounds are oxidized either chemically (6), photochemically (7) or biologically, the predominent reaction is the rupture of the N-C bond. Compounds such as IDA (iminodiacetic acid) and oxalic acid have been isolated. An anticipated overall reaction pathway based on such a sequence is shown in Fig. 6. Complete oxidation of NTA would proceed via eq. 6 and 7 which combine to the overall equation 8.

$$6\ FeO_4^{=} + 30\ H^{+} + N(CH_2COOH)_3 \rightarrow 6\ CO_2 + NH_3 + 6\ Fe^{+3} + 18\ H_2O \quad (6)$$

$$NH_3 + FeO_4^{=} + 5\ H^{+} \rightarrow \tfrac{1}{2}\ N_2 + Fe^{+3} + 4\ H_2O \quad (7)$$

$$7\ FeO_4^{=} + 35\ H^{+} + N(CH_2COOH)_3 \rightarrow 6\ CO_2 + \tfrac{1}{2}\ N_2 + 7\ Fe^{+3} + 22\ H_2O \quad (8)$$

Preliminary experiments showed that the kinetics of the NTA reaction are very complicated when ferrate ion is added in excess or in stoichiometric equivalent amount. It is observed that, for $C_{NTA} = 0.10$ at pH 9, a 6:1 reactant ratio of ferrate:NTA proceeds rapidly to complete reduction of ferrate ion but a 7:1 ratio proceeds rapidly at first but then virtually stops with a considerable amount of ferrate remaining.

NTA and oxalic acid oxidations were sufficiently slow that they were studied by conventional spectrometry. IDA, glycine and glyoxylic acid, on the other hand, were oxidized so rapidly that stopped-flow spectrophotometry was required. In all cases, the rate law is in accord with equation 5 and k_1 and k_2 are not changed from the values measured in the absence of the solutes. Tables4-8 give values of rate constants obtained in these reactions.

The rate constants of oxidation of these solutes and of water allow the calculation of the concentration of each substrate which would give a rate

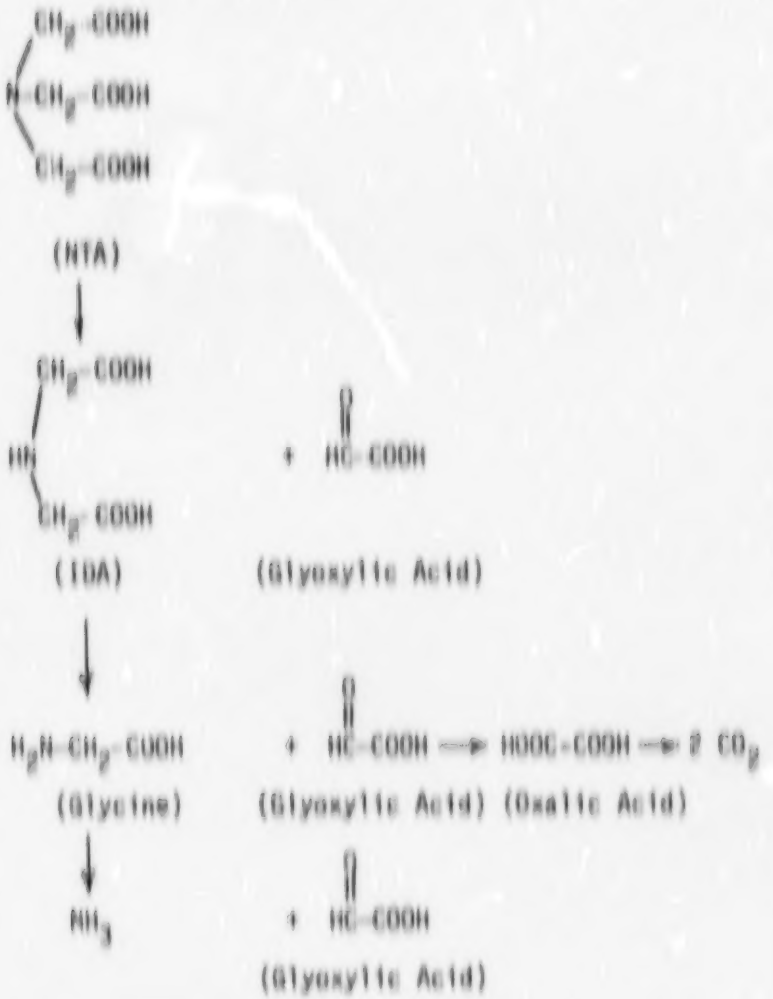

Figure 6. Proposed Reaction Pathways for the Potassium Ferrate Oxidation of NTA.

equal to the water oxidation rate at any pH and ferrate concentration. Table 9 includes this information for pH 6.80 and $[FeO_4^{=}] = 8.0 \times 10^{-4}$ M.

The hydrogen ion dependence of these reactions are analyzed in terms of different reactivities of the different protonated forms of the solute molecules. The usual graphical methods are employed and the results are shown in Table 10. An alternate approach which did not seem appropriate would be to assign the pH dependence to different protonated forms of ferrate ion, $FeO_4^{=}$, $HFeO_4^{-}$ and $Fe_2O_7^{=}$. The latter two species have never been observed although their presence has been the subject of speculation (8).

The fate of the nitrogen atom of NTA in these ferrate oxidations is of interest. Figure 6 suggests that ammonia may be formed after the successive rupture of the three N-C bonds. The oxidation of ammonia therefore is of interest. Ammonia is often found at low concentrations in contaminated waters and is a source of oxygen demand that is not included in the conventional dichromate COD determination. There are old references that suggest that ferrate ion will oxidize ammonia to molecular nitrogen (9).

The ferrate oxidation of ammonia was monitored by both spectrophotometry ($-d[FeO_4^{=}]/dt$) and by voltammetric oxygen electrode ($d[O_2]/dt$) and the results are given in Table 11.

The very complicated kinetics of this system can be summarized as follows:

1. The oxidation of dilute aqueous ammonia to form N_2 is a very minor pathway.
2. The rate of ferrate disappearance has an order between first and second in analytical concentration of ammonia.
3. The rate of ferrate disappearance is essentially equal to the rate of oxygen appearance (after correction for stoichiometry).

The general conclusion therefore is that ammonia catalyzes the oxidation of water but only a small fraction of the ammonia is actually oxidized itself. Mass spectral study of the volatile products do indicate a small amount of N_2, but it is much less than the O_2 which is observed.

Detailed interpretation of the ammonia oxidation is complicated but yields eq. 9.

$$\text{rate} = \frac{-d[FeO_4^{=}]}{dt} = (k_a[NH_4^{+}] + k_b[NH_3])\,[FeO_4^{=}] + ((k_{2Na}[NH_4^{+}] + k_{2N0}[NH_3]^2)\,[H^{+}] + k_2)\,[FeO_4^{=}]^2 \qquad (9)$$

Numerical values of the rate constants in eq. 9 at 25°C in the previously described phosphate-borate buffer are $k_a = 0.14\ \underline{M}^{-1}\ sec^{-1}$, $k_b = 0.12\ \underline{M}^{-1}\ sec^{-1}$, $k_{2Na} = 3.5 \times 10^{11}\ \underline{M}^{-3}\ sec^{-1}$, $k_{2N0} = 2.6 \times 10^{13}\ \underline{M}^{-4}\ sec^{-1}$ and k_2 represents the uncatalyzed reaction and retains the value shown for it in an earlier section.

Organic Amines

The four organic amines selected for study; triethylamine, diethylamine, piperidine and pyridine are simple representative of tertiary alkyl, secondary alkyl, cyclic alkyl and aromatic classes of amines. The relationship of the structures of triethylamine and diethylamine to NTA and IDA respectively is noted. Table 12 gives values of rate constants, resolved as described by eq. 3, for these systems. Only minor differences in the rate constant for water oxidation are observed in the presence of these amines (see values of k_2^{PR}). The psuedo-first order rate constants are interpreted as being actual oxidations of the organic amines. This conclusion is supported by use of the oxygen probe in the diethylamine oxidation. Only 40% of the ferrate was reduced in the formation of O_2; the remaining 60% presumably oxidized the amine.

the pH dependence of k_1^{PR} shows a term which is first-order in hydrogen ion to be the predominant reaction pathway. Values of the substrate oxidation rate constant, k_s, in these cases are 3.22×10^4 M^{-1} sec^{-1} (triethylamine), 2.08×10^6 (diethylamine) and 2.9×10^6 (piperazine).

Two Carbon Compounds

The two carbon compounds examined, ethanol, acetaldehyde and acetate ion represent a progression of increasing oxidation number of one of the carbon atoms. It should be noted that the di-functional two-carbon compounds, glyoxylic and oxalic acids, were mentioned in an earlier section.

Ethanol oxidation is quite straight-forward, following a rate law as shown in eq. 5. Values of the conditional rate constants are given in table 13.

Acetaldehyde oxidation is very complicated. The tendency for its basic aqueous solutions to undergo an aldol condensation followed by dehydration or further polymerization cause the oxidation kinetics to depend strongly on the history of the sample. The reaction is first-order in ferrate ion but can be one-half-order or first-order in acetaldehyde, depending on pH, concentration and solution age.

Acetate ion is not oxidized by ferrate ion. Even very high concentration of acetate ion at pH and exhibit the same rate of ferrate disappearance as does a blank solution with only phosphate-borate buffer.

FERRATE ION IN OXYGEN DEMAND MEASUREMENT

Standard phenol, lactic acid, pyridine and ammonia samples were subjected to the conventional sulfuric-dichromate COD analysis. Virtually quantitative oxidation to form CO_2 were observed with phenol and lactic acid

and no oxidation of either pyridine or ammonia were observed. This is in keeping with the earlier observations of Moore et al. (10). Since the lack of reactivity of ferrate ion with pyridine and ammonia had already been demonstrated, they were not tested further in conjunction with COD determination.

Lake water (Random Lake, Wisconsin) and both raw sewage and treated effluent from the Lincoln, Nebr. sewage treatment plant were tested for COD level. Several portions of filtered raw sewage (COD = 49 ppm) were treated with K_2FeO_4 and the COD remeasured after the ferrate had been completely reduced. The resulting treated sewage showed a COD of 170 ± 20 ppm. This was entirely unsuspected, it being anticipated that the COD would decrease. When unfiltered raw sewage was used in similar experiments, the COD decreased from 377 to 110 ppm if pH was not controlled and from 377 to 273 ppm if the pH was held at 7.46 with phosphate-borate buffer. The $Fe(OH)_3$ formed as the reduction product presumably removed oxidizable solids from the unfiltered sewage. This behavior was not as important in the buffered sewage since the Fe(III) is largely held in solution as the soluble phosphate and borate complexes.

The increase in measured COD of sewage samples after ferrate treatment is tentatively attributed to the labilization by ferrate ion of polymeric organic compounds, such as humic materials, which are unreactive to the conventional COD assay.

TABLE I

EXPERIMENTAL FIRST- AND SECOND-ORDER RATE CONSTANTS FOR THE POTASSIUM FERRATE OXIDATION OF WATER

T = 25.0° phosphate-borate buffer

pH	$[FeO_4^{2-}]_o$ range ($\times 10^4$)	$k_2^{H_2O}$ (sec^{-1} M^{-1})[a]	$k_1^{H_2O}$ ($\times 10^3$ sec^{-1})[a]
7.85	8.09-11.81	27.0 ± 3.1	3.49 ± 0.97
7.85	1.40	19.8 ± 2.3	11.4 ± 1.2
8.00	11.44-15.64	15.9 ± 2.2	1.67 ± 0.31
8.00	1.08	12.7 ± 2.4	4.97 ± 0.76
8.15	6.88-15.73	8.30 ± 0.10	1.13 ± 0.05
8.15	0.735	4.41 ± 1.04	4.12 ± 0.32
8.30	8.25-9.71	4.76 ± 0.66	
8.30	0.726	3.41 ± 0.82	2.31 ± 0.24
8.45	8.87-15.78	2.74 ± 0.12	
8.60	9.72- 9.51	1.50 ± 0.22	
8.79	11.00-16.24	0.92 ± 0.11	
8.95	8.15-12.20	0.48 ± 0.06	
9.04	12.72-17.23	0.36 ± 0.07	
8.15	7.0 -12.0	3.95	
8.45	7.0 -12.0	1.62	
8.79	7.0 -12.0	0.445	
9.04	7.0 -12.0	0.158	

a. Mean value ± standard deviation of a measurement.

TABLE 2

RATE CONSTANTS FOR FERRATE OXIDATION OF METHYL ALCOHOL

T = 25°C, phosphate-borate buffer

$k_{obs} = k_1 + k_s [CH_3OH]$

Run No.	pH	$[CH_3OH]_o$	$[FeO_4^{=}]_o$ x 10^3	k_{obs} $(sec^{-1})x10^4$	k_s $(M^{-1}sec^{-1})x10^4$
10	7.92	0.370	1.71	283	
11	7.94	0.272	1.93	224	
7	7.98	0.721	1.15	505	
8	7.98	0.365	1.44	229	
6	7.99	0.745	1.46	404	
12	8.08	0.663	0.711	195	
13	8.08	0.221	0.924	102	
30	8.40	0.145	0.850	32.4	
29	8.41	0.290	0.629	54.0	
27	8.42	1.452	0.695	230	
28	8.46	0.871	1.24	127	
52	8.69	1.106	1.09	131	
53	8.68	0.663	0.843	78.0	
54	8.69	0.221	0.874	32.4	
55	8.70	0.111	0.940	19.9	
19	8.89	1.452	0.970	99.3	
20	8.93	0.871	1.34	56.0	
21	8.92	0.290	0.777	20.7	
22	8.94	0.145	0.751	10.2	
23	8.91	1.452	1.01	104	
24	8.88	0.871	0.682	63.0	
25	8.96	0.290	1.470	20.7	
40	9.32	1.106	9.609	31.2	
41	9.32	1.106	0.960	29.0	
42	9.32	1.106	0.816	32.0	
36	9.41	1.105	0.497	25	
37	9.46	0.664	1.23	17.9	
38	9.44	0.221	0.860	7.29	
39	9.44	0.111	0.868	4.33	
1	10.13	1.873	24.0	4.98	
9	10.81	0.963	1.09	3.18	
32-35	8.09				208
27-30	8.42				137
52-55	8.69				114
19-22	8.91				68.0
23-25	8.93				72.0
37-39	9.44				24.8
2-7 (CG)	9.10				46

TABLE 3

RATE CONSTANTS FOR FORMATE ION OXIDATION BY FERRATE ION

T = 25°C phosphate-borate buffer

Run No.	pH	$[HCOO^-]_0 \times 10^2$	$[FeO_4^{2-}]_0 \times 10^3$	k_s (sec^{-1}) $\times 10^3$
16	7.80	0.203	0.833	1.9
17	7.80	0.406	0.833	14.8
18	7.80	0.606	0.833	9.38
19	7.80	0.813	0.833	10.5
20	7.80	1.616	0.833	11.9
21	7.80	1.996	0.833	19.4
22	7.80	0.833	0.833	23.0
40-1	8.12	1.03	0.833	6.92
40-2	8.12	1.03	0.833	7.08
41-1	8.12	2.06	0.833	17.6
41-2	8.12	2.06	0.833	19.6
42-1	8.12	3.09	0.833	14.6
42-2	8.12	3.09	0.833	15.5
43-1	8.12	4.11	0.833	16.2
43-2	8.12	4.11	0.833	16.4
24	8.78	0.206	0.833	0.275
25	8.78	0.411	0.833	0.542
26	8.78	0.617	0.833	0.788
27	8.78	0.823	0.833	1.04
28	8.78	1.03	0.833	1.20
29	8.78	2.06	0.833	2.12
30	8.78	3.09	0.833	2.85
31	8.73	4.11	0.833	3.74
11	9.30	0.203	0.833	0.16
13	9.30	0.609	0.833	0.77
14	9.30	0.813	0.833	0.76
5	9.32	1.02	0.833	0.55
9	9.30	2.03	0.833	1.01
7	9.32	3.05	0.833	1.54
8	9.32	4.06	0.833	1.55
32	9.80	0.206	0.833	0.164
33	9.80	0.411	0.833	0.411
34	9.80	0.617	0.833	0.417
35	9.80	0.823	0.833	0.506
36	9.80	1.03	0.833	0.607
37	9.80	2.06	0.833	1.07
38	9.80	3.09	0.833	1.48
39	9.80	4.11	0.833	1.66
46	9.30	4.11	0.020	1.85
10	9.30	4.06	0.833	1.07
1	9.36	1.02	0.833	0.50

TABLE 3 (continued)

T = 25°C phosphate-borate buffer

Run No.	pH	$[HCOO^-]_0 \times 10^2$	$[FeO_4^=]_0 \times 10^3$	k_s (sec^{-1}) $\times 10^3$
2	9.14	2.03	0.833	0.98
3	8.65	1.48	0.833	1.6
4-3	8.07	4.06	0.833	20.
4-6	8.09	4.06	0.833	20.
6	9.49	2.03	0.833	0.8
10	9.30	4.06	0.833	1.07

TABLE 4

RATE CONSTANTS FOR THE FERRATE OXIDATION OF NITRILOTRIACETIC ACID

$T = 25.0°$ phosphate-borate buffer

pH	k_s^{NTA} (sec^{-1} M^{-1})
8.15	2.037 ± 0.053
8.32	1.938 ± 0.045
8.47	1.814 ± 0.043
8.65	1.702 ± 0.042

TABLE 5

RATE CONSTANTS FOR FERRATE OXIDATION OF IMINODIACETIC ACID

T = 23° phosphate-borate buffer

pH	$[IDA]_o \times 10^2$	$[FeO_4^{2-}]_o \times 10^4$	k_{Obs} (sec^{-1})	k_2^{IDA} ($sec^{-1}\ M^{-1}$)
8.60	1.535	8.65	0.930	60.6
8.80	1.52	6.555 8.48	0.652 ± 0.036	42.9 ± 2.4
9.20	1.485	7.80 7.85	0.360 ± 0.024	23.6 ± 1.6
9.40	1.425	7.70	0.198 ± 0.015	13.9 ± 1.0

TABLE 6

RATE CONSTANTS FOR FERRATE OXIDATION OF GLYCINE

$t = 23°C$ phosphate-borate buffer

pH	$[GLY]_o \times 10^2$	$[FeO_4^=]_o \times 10^4$	k_{Obs} (sec^{-1})	k_s^{GLY} ($sec^{-1}\ M^{-1}$)
8.50	1.635	8.45	0.958	60.6
8.80	1.62	6.02 7.75	0.958 ± 0.120	59.1 ± 7.4
9.20	1.60	4.84 5.765 6.685	0.884 ± 0.085	55.3 ± 5.3
9.40	1.565	8.15	0.724 ± 0.036	46.3 ± 2.3

TABLE 7

OBSERVED RATE CONSTANTS FOR FERRATE OXIDATION OF GLYOXYLIC ACID

T = 25.0°C phosphate-borate buffer

pH	$[GLA]_o \times 10^2$	$[FeO_4^{2-}]_o \times 10^4$	k_{Obs} (sec^{-1})
8.80	1.245	6.20 8.15	7.900 ± 0.630
9.00	1.225	5.60 7.95	8.256 ± 0.688
9.20	1.225	5.55 7.80	7.825 ± 0.371
9.40	1.230	5.95 8.35	7.532 ± 0.426

TABLE 6

RATE CONSTANTS FOR FERRATE OXIDATION OF OXALATE

T = 25.0°C phosphate-borate buffer

pH	k_s (sec^{-1} M^{-1})
7.85	0.650 ± 0.042
8.00	0.351 ± 0.035
8.15	0.174 ± 0.013
8.30	0.104 ± 0.006
8.66	0.0109 ± 0.0006

TABLE 9

SUBSTRATE CONCENTRATIONS NEEDED FOR RATE OF OXIDATION TO EQUAL WATER OXIDATION RATE[a]

Substrate	k_2^{SUB} (sec^{-1} M^{-1})	[SUB] to cause Rate = Rate of Water Oxidation
NTA	1.60	.00045
IDA	42.9	.000017
Glycine	55.1	.000012
Oxalic Acid	0.015	.048
Glyoxylic Acid	635	.0000011

a. Rate of water oxidation, at pH 8.80, is 5.76×10^{-7} M sec^{-1}, $[FeO_4^{=}] = 8 \times 10^{-4}$.

TABLE 10

RESOLVED RATE CONSTANTS FOR PROTONATED FORMS OF SOME SUBSTRATES

25°C phosphate-borate buffer

formic acid		
	HA	6.05×10^{3} M^{-1} sec^{-1}
	A^-	4×10^{-7} M^{-1} sec^{-1}
oxalic acid		
	H_2Ox	1.15×10^{10} M^{-1} sec^{-1}
	HOx^-	2.75×10^{2} M^{-1} sec^{-1}
	$Ox^{=}$	~ 0
glycine		
	H_2gly^+	~ 0
	$Hgly^{\pm}$	65 M^{-1} sec^{-1}
	gly^-	~ 0
iminodiacetic acid		
	H IDA$^-$	~ 65 M^{-1} sec^{-1}
	$IDA^{=}$	~ 0
nitrilotriacetic acid		
	H_2NTA^-	8×10^{4} M^{-1} sec^{-1}
	$HNTA^{2-}$	1.59 M^{-1} sec^{-1}
	NTA^{3-}	~ 0
glyoxylic acid		
	HG	~ 0
	G^-	627 M^{-1} sec^{-1}

TABLE 11

RATE CONSTANTS FOR AMMONIA OXIDATION BY FERRATE ION

T = 25°C phosphate-borate buffer

Run No.	pH	C_{NH_3} x 10^3	$[FeO_4^{=}]_o$ x 10^3	k_{obs} ($M^{-1}sec^{-1}$) x 10^4	k_1 (sec^{-1}) x 10^3	k_2 ($M^{-1}sec^{-1}$) x 10^4
41	8.33	0.051	.689	39.3		
40	8.33	0.051	1.33	18.8		
47	8.33	0.510	0.554	62.4		
36	8.97	0.	1.73	2.07		
32	8.97	0.051	0.604	5.46		
31	8.97	0.051	1.33	2.85		
35	8.97	0.051	1.55	2.45		
37	8.97	0.510	6.09	7.65		
38	8.97	0.510	0.726	5.45		
51	9.36	0.	1.55	0.579		
49	9.36	0.051	1.61	0.648		
43	9.84	0.	1.32	0.190		
45	9.84	0.051	0.650	0.429		
42	9.84	0.051	1.60	0.284		
48	9.84	0.510	0.502	2.21		
46	8.28	10.2	0.510		1.19	18.1
39	8.85	10.2	0.543		1.24	3.30
101	9.17	10.2	0.703		1.44	2.12
50	9.17	10.2	0.610		1.24	2.03
44	9.50	10.2	0.720		1.16	1.15
58	8.24	20.4	0.641		2.52	5.29
59	8.65	30.6	0.683		3.43	10.7
60	8.60	40.8	0.743		4.74	45.8
61	9.33	20.4	0.631		2.29	8.34
62	9.21	30.6	0.583		3.44	21.2
63	9.12	40.8	0.655		4.47	39.9

TABLE 12

REACTION CONDITIONS AND VALUES OF k_{obs}, k_1^{PR} and k_2^{PR} FOR REACTIONS BETWEEN POTASSIUM FERRATE AND VARIOUS AMINES

All Reactions Employed $[FeO_4^{=}]_0 = 6.78 \times 10^{-4}$ M

A. Stoichiometric Reactions: $[Amine]_0 = 1.08 \times 10^{-3}$ M

Rx. #	pH	$[H^+] \times 10^9$	$k_{obs} \times 10^3$	$k_1^{PR} \times 10^3$	k_2^{PR}
		Triethylamine - $(C_2H_5)_3N$			
15	7.55	28.2	15.8	****	***
12	8.23	5.89	2.92	0.733	11.0
11	8.51	3.09	1.60	0.781	3.69
10	9.03	0.933	0.699	0.591	0.361
13	9.47	0.339	0.478	0.543	***
14	9.94	0.115	0.456	0.618	***
		Piperidine - $(C_5H_{10})NH$			
27	9.44	0.363	2.63	2.96	***
29	9.92	0.120	1.87	2.24	***
		Pyridine - $(C_5H_5)N$			
30	9.00	1.00	0.130	0.011	0.467
		Diethylamine - $(C_2H_5)_2NH$			
22	8.23	5.89	3.57	1.96	7.67
21	8.50	3.16	2.05	1.41	2.70
19	9.03	0.933	0.989	.967	0.415
18	9.44	0.363	0.735	0.765	0.357
20	9.94	0.115	0.653	0.779	***

TABLE 12 (continued)

B. Amine Dependent Reactions Using Diethylamine

Rx. #	pH	$[(C_2H_5)_2NH] \times 10^3$	$k_{obs} \times 10^3$
21	8.50	1.08	2.09
23	8.48	2.11	2.7[illegible]
24	8.48	4.04	3.80
25	8.48	5.79	4.58
26	8.48	8.88	5.83

TABLE 13

RATE CONSTANTS FOR ETHYL ALCOHOL OXIDATION BY FERRATE ION

T = 25°C phosphate-borate buffer

Run No.	pH	$[EtOH]_o$	$[FeO_4^{=}]_o$ x 10^3	k_{obs} $(sec^{-1})\times10^3$	k_s $(M^{-1}sec^{-1})$
1	9.36	0.400	0.86		
2	9.12	0.300	0.96	1.61	
3	9.10	0.200	1.06	1.44	
4	9.09	0.100	0.96	1.04	
5	9.08	0.020	1.11	0.556	
6	9.06	0.010	1.08	0.338	
11	8.59	0.400	1.01	4.97	
12	8.46	0.300	1.31	4.91	
13	8.43	0.200	0.96	3.62	
14	8.39	0.160	1.31	3.06	
15	8.41	0.100	1.26	3.41	
16	8.42	0.060	1.41	3.37	
17	8.42	0.050	1.62	2.93	
18	8.36	0.011	0.96	2.43	
21	8.55	0.300	1.06	4.47	
22	8.56	0.200	1.26	3.50	
23	8.53	0.160	1.21	3.22	
24	8.51	0.060	1.16	2.32	
25	8.20	0.300	1.06	6.52	
26	8.25	0.200	1.01	5.55	
27	8.26	0.160	1.21	5.26	
28	8.23	0.060	1.06	3.77	
29	9.10	0.300	1.31	2.46	
30	9.08	0.200	0.91	1.70	
31	9.10	0.160	1.16	1.52	
32	9.60	0.400	1.16	1.99	
33	9.60	0.300	1.11	1.56	
34	9.59	0.200	1.21	1.09	
35	9.90	0.400	1.11	1.25	
36	10.07	0.300	1.24	1.02	
37	10.03	0.200	1.14	0.733	
25-28	8.20-8.26				106
11-16	8.36-8.46				71.6
21-24	8.51-8.56				66.9
29-31	9.08-9.10				80.9
32-34	9.59-9.60				45.1
35-37	9.90-10.07				25.3

TABLE 14

RATE CONSTANTS FOR OXIDATION OF ACETALDEHYDE BY FERRATE ION

t = 25.0° phosphate-borate buffer

Run No.	pH	$[CH_3CHO]_o$	$[FeO_4^{=}]_o \times 10^3$	k_{obs} (sec^{-1}) $\times 10^3$
1	8.70	0.200	1.25	200
5	8.93	0.110	1.22	109
6	9.02	0.040	0.458	40
7	9.04	0.013	0.881	10
8	9.11	0.400	1.02	28.0
9	9.08	0.300	0.661	24.2
10	9.09	0.200	1.20	16.9
11	9.09	0.160	0.915	18.8
12	9.12	0.100	0.848	13.1
13	9.12	0.060	0.610	8.85
14	9.07	0.050	0.627	7.73
15	9.12	0.030	0.559	6.93
16	9.18	0.018	0.780	3.5
17	10.48	0.400	0.814	14.3
18	10.54	0.160	0.814	7.21
19	10.57	0.018	0.814	1.65
20	9.27	0.400	0.678	26.3
21	9.29	0.160	0.712	12.8
22	9.33	0.018	0.678	2.32
24	8.02	0.160	0.848	128
25	8.04	0.018	0.610	15.4
26	9.88	0.400	0.661	14.3
27	9.94	0.160	0.661	7.39
28	9.97	0.018	0.729	1.51
29	9.20	0.400	0.644	26.2
30	9.23	0.160	0.695	12.9
31	9.26	0.0020	0.627	0.145
32	8.52	0.400	0.678	58.6
33	8.52	0.160	0.712	37.2
34	8.56	0.018	0.644	7.03
35	9.22	0.018	0.678	2.34
36	9.09	0.0050	0.0630	0.468
37	8.99	0.0020	0.0679	0.220
38	8.98	0.00050	0.0533	0.116
39	9.00	0.00005	0.0485	0.088
41	9.17	0.030	0.567	0.856
42	9.16	0.012	0.523	0.792
43	9.14	0.0080	0.0533	0.297
44	9.14	0.0040	0.0436	0.206
45	9.14	0.0020	0.0485	0.177
46	9.14	0.060	0.465	1.06
47	9.12	0.060	0.0630	2.29
48	8.91	0.060	0.494	4.74

TABLE 14 (continued)

Run No.	pH	$[CH_3CHO]_0$	$[FeO_4^{=}]_0 \times 10^3$	k_{obs} (sec^{-1}) $\times 10^3$
49	9.14	0.060	0.504	2.77
50	9.14	0.060	0.519	3.12
51	9.14	0.060	0.514	3.28
52	9.14	0.060	0.499	3.40
53	8.96	0.0299	0.959	3.53
54	9.12	0.0299	1.11	2.76
55	9.11	0.0299	1.01	2.63
56	9.13	0.0299	1.06	2.14
57	9.11	0.0299	1.26	2.73
58	9.11	0.0299	0.909	3.00
59	8.84	0.0299	0.727	3.61
60	8.99	0.0299	0.824	2.49
61	9.00	0.0299	0.824	2.50
62	9.00	0.0299	0.897	2.72
63	8.85	0.0299	0.593	3.16
64	8.98	0.0299	0.678	2.42
65	9.08	0.0299	0.800	1.39
66	9.09	0.0299	0.945	0.581
67	9.12	0.0299	0.824	0.460

TABLE 15

COD VALUES FOR ALL WASTEWATER AND LAKE WATER SAMPLES

Sample #	Type of Sample*	K_2FeO_4 Added (mg)	COD mg O_2/l
54	lake water	-------	26.38
56a	lake water	---------	31.28
56b	lake water	4.3	27.20
64	final effluent	---------	32.31
65	final effluent w/o chlorination	---------	31.93
66	raw sewage	---------	377.50
77	filtered raw	---------	31.55
78	filtered raw	---------	76.41
81	filtered raw	---------	46.48
82	filtered raw	---------	46.48
83	filtered raw	---------	52.72
67	raw sewage	32	179.63
73	filtered raw	32	191.03
79	filtered raw	32	156.16
71	raw sewage	7.8	110.06
72	raw sewage + 5 ml pH = 7.46 buffer	7.8	273.14
75	filtered sewage + 5 ml pH = 9.45 buffer	7.8	49.04
74	filtered raw	7.8	67.10
84	filtered raw	7.8	52.32
85	filtered raw	7.8	49.92

TABLE 15 (continued)

Sample #	Type of Sample*	K_2FeO_4 Added (mg)	COD mg O_2/l
86	filtered raw	7.8	47.52
86a	20 ml filtered raw	15.6	28.56
86b	10 ml from #86a	7.8	130.40
86c	5 ml from #86b	4.1	66.05
88a	20 ml filtered raw	15.0	21.68
88b	10 ml from #88a	7.6	48.80
88c	5 ml from #88b	3.8	131.84

*All sample volumes were 10 ml except where otherwise specified

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16. ABSTRACT

This research project was initiated with the primary objective of improving the commonly used COD test by the use of ferrate(VI) ion as an alternate or preliminary oxidant. The oxidation of NH_3 and more general oxidation of organic compounds was desired. A secondary objective was the improved understanding of the mechanism of ferrate oxidations in dilute aqueous solutions.

The oxidation kinetics of water (phosphate-borate buffer) by ferrate ion were studied spectrophotometrically and by oxygen evolution measurements. The kinetics of ferrate oxidation of methanol, formic acid, ethanol, acetaldehyde, acetic acid, NTA, IDA, glycine, glyoxalic acid, oxalic acid, triethylamine, diethylamine and piperidine were examined and are described.

The dichromate COD analysis was carried out on several samples, including phenol, lactic acid and sewage from the Lincoln, Nebraska sewage treatment facility. COD analysis was also carried out on sewage samples after prior treatment with potassium ferrate at pH 9. There was evidence that the ferrate ion actually labilized organic materials originally refractory to the dichromate COD method but the oxidation of water (possibly catalyzed by sewage components) is too rapid to insure that the ferrate reacts quantitatively with the solute molecules. It is concluded, therefore, that the COD test cannot be improved significantly by the incorporation of ferrate(VI) ion as an oxidant.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Ferrate Water analysis Oxidation	Chemical oxygen demand (COD) Potassium ferrate Catalytic	07B

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